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Electrochemical study of copper and bismuth compounds in the solid state by using voltammetry of immobilized microparticles: application to $\text{YBa}_2\text{Cu}_3\text{O}_{7-x(s)}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-x(s)}$ high transition temperature superconductors

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Abstract In this paper, an electrochemical study was carried out of different solid samples, such as $\text{Cu}_2\text{O}_{(s)}$, $\text{CuO}_{(s)}$, $\text{Bi}_2\text{O}_{3(s)}$ and $\text{NaBiO}_{3(s)}$ and their binary mixtures, in order to characterize the high transition temperature superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{7-x(s)}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-x(s)}$. These studies were carried out by using an electrode with a glassy tube and a plastic piston, containing a mass of carbon paste bound with liquid paraffin. The technique employed in our paper is similar to that developed by others.

Keywords Voltammetry of immobilized microparticles · Copper compounds · Bismuth compounds · Superconductors

Introduction

Electrochemical studies of solids were carried out at the end of the last century by Glazunov and by Scholz, using an electrographic technique, although only from a qualitative point of view [1]. Adams [2] in the USA, as well as others authors such as Lecuire [3] in France, have studied different solids by the use of carbon paste composite electrodes. More recently, Scholz et al. [4, 5, 6, 7, 8, 9, 10, 11] in 1989 developed a new electrochemical technique, called “voltammetry of immobilized microparticles”, for solid studies, where scan rates are comparable to the ones used in solution voltammetry. On the other hand, by using composite electrodes, we have studied different solid compounds, using different oxides such as $\text{Cu}_2\text{O}_{(s)}$, $\text{CuO}_{(s)}$, $\text{Bi}_2\text{O}_{3(s)}$ and $\text{NaBiO}_{3(s)}$ and their mixtures, in

order to characterize high transition temperature superconductors, such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-x(s)}$ [12] and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-x(s)}$ [13]. Much more recently, Cha et al. [14, 15] and Vivier [16] made a cavity microelectrode which was utilized to study solid compounds.

The most important problem concerning carbon paste composite electrodes, when employed to study solid compounds by the use of electrochemical techniques, is the low scan rate that it is necessary to employ. Nevertheless, this problem was minimized by the use of the “voltammetry of immobilized microparticles” electrochemical technique developed by Scholz et al. [4]. This technique utilizes a paraffin-impregnated graphite cylinder as the electrode. To fix the solid sample particles on the top of this cylinder, it is necessary to brush the sample distributed on a hard surface. On the other hand, to electrolyse these particles it is only necessary to touch the solution with the surface of the working electrode. The other electrodes, the reference and auxiliary electrodes, can be classically introduced in the electrolyte. Concerning the cell, a classic design was utilized.

In this paper, we describe our studies on the electrochemical reactions of solid samples, such as $\text{Cu}_2\text{O}_{(s)}$, $\text{CuO}_{(s)}$, $\text{Bi}_2\text{O}_{3(s)}$ and $\text{NaBiO}_{3(s)}$ and their binary mixtures, in order to characterize high transition temperature superconductors, e.g. $\text{YBa}_2\text{Cu}_3\text{O}_{6.92(s)}$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.75(s)}$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.44(s)}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8(s)}$.

Experimental

Apparatus

In order to obtain I versus E curves, a PSTAT 10 Autolab (Eco-Chemie) and GPES 4.4 software were utilized.

Electrodes and reagents

A saturated calomel electrode (SCE) was used as the reference electrode, a Pt wire as the auxiliary electrode and a carbon paste Metrohm EA-267 (6.0802.000) with a piston as the working electrode. To

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prepare this working electrode, the whole of the Metrohm device was refilled with a home-made carbon paste. In this case the Metrohm hole had a height of 3 cm with a 6.95 mm inner diameter. The optimal ratio of C/Nujol oil was 2 g of C/0.5 mL of Nujol oil. In order to polish the carbon paste surface of the electrode tip, a rotation movement was carried out on a suitable surface.

Spectroscopically pure graphite (ultrapure carbon, UPC) of particle size 200 mesh was supplied by Carbon of America (Bay City, Mich., USA). All the reagents were of analytical grade and supplied by Carlo Erba and Merck.

The samples of the superconductors were provided by Prof. M. A. Alario of the Inorganic Department of the Complutense University of Madrid (Spain).

Procedure

To incorporate samples into the working electrode, a little thoroughly ground amount of solid (0.4 mg) was spread over a hard Perspex surface, and by rubbing on that spot the solid sample was incorporated into the electrode. After transporting the solid sample on the tip of the electrode, according to Scholz et al. [4], the tip of the electrode surface was brought into contact with the surface of the solution. The other electrodes were introduced classically into the working solution. A scheme of the electrolytic cell can be seen in Fig. 1.

The scan rate in all cases was 10 mV/s. In order to polish the tip of the carbon paste electrode, the surface was rubbed on a filter paper surface before each measurement.

Results and discussion

The voltammograms of the studied compounds were always carried out by starting from its characteristic open circuit potential ($E_{(i=0)}$) and the following scan types were recorded: (1) cathodic scans up to -1.5 V followed by an anodic scan up to 0.5 V and several cyclic potential scans; (2) anodic scans up to 0.5 V followed by a cathodic scan up to -1.5 V and several cyclic scans. Potential values between -1.5 V and 0.5 V were the electroactivity limits of the utilized media.

Voltammetric study of Cu(I) and Cu(II) compounds in 10 M KOH media

Voltammograms of $\text{Cu}_2\text{O}_{(s)}$

Different voltammograms of $\text{Cu}_2\text{O}_{(s)}$, obtained by potential scans from -0.390 V, are plotted in Fig. 2. If the first scan was cathodic (Fig. 2a), peak C_1 (-1.280 V)

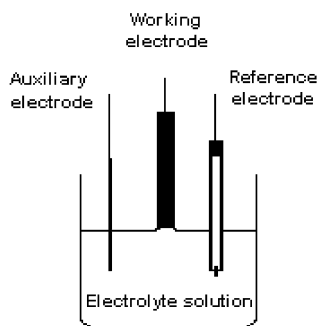


Fig. 1 The electrochemical cell

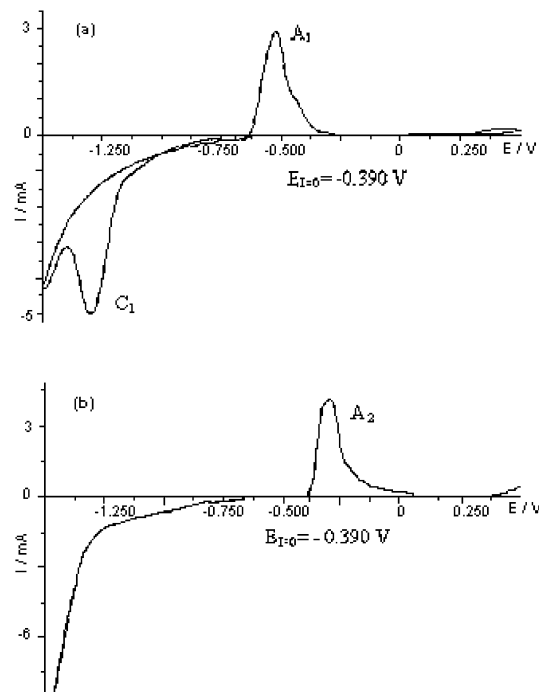


Fig. 2a,b Voltammograms of Cu_2O . a First scan towards negative potential values. b First scan towards positive potential values

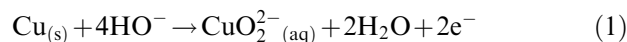
appeared; in the return anodic scan, peak A_1 (-0.560 V) also appeared. When the first scan was started in the anodic direction, Fig. 2b was obtained in which only peak A_2 (-0.290 V) appeared, and no peak was obtained in the following cathodic scan. No signal was observed during the subsequent cyclic scans.

Voltammograms of $\text{CuO}_{(s)}$

The voltammograms of $\text{CuO}_{(s)}$, obtained by scanning the potential from -0.135 V, are plotted in Fig. 3. When the first scan was cathodic (Fig. 3a), peak C_2 (-1.139 V) was obtained; in the return anodic scan, peak A_1 (-0.560 V) appeared. In Fig. 3b it can be observed that in the first anodic scan no signal was obtained, although the peaks C_2 (-1.139 V) and A_1 (-0.560 V) were recorded in the return cathodic scan and in the second anodic scan, respectively, but no signal was observed in subsequent cyclic scans.

From the experimentally obtained results, it can be deduced that:

1. The anodic peak A_1 , which appeared at the same potential value for both compounds, is attributable to the following electrochemical process:



2. The cathodic peak C_1 , which only appeared when the only species on the electrode was $\text{Cu}_2\text{O}_{(s)}$, can be attributable to the following electrochemical reaction:

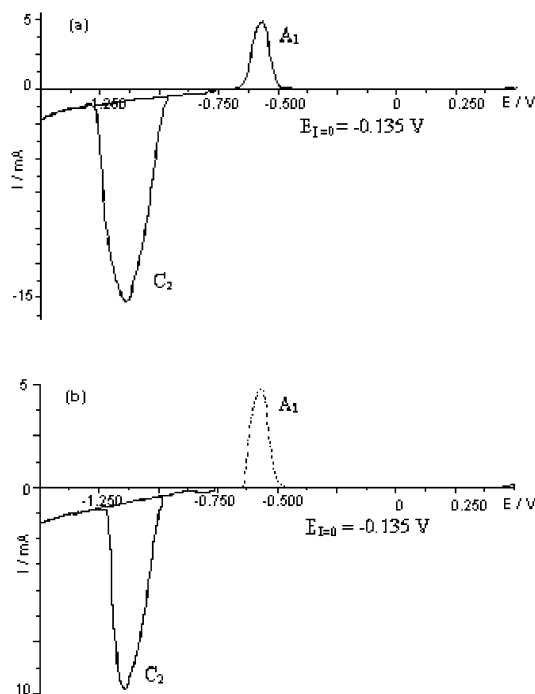
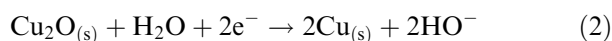
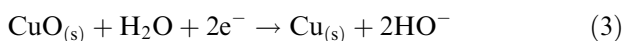


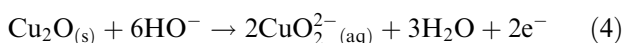
Fig. 3a,b Voltammograms of CuO. **a** First scan towards negative potential values. **b** First scan towards positive potential values. Full line: first cyclic scan; dashed line: second cyclic scan



3. The cathodic peak C_2 , which only appeared if the chemical species on the electrode was $\text{CuO}_{(s)}$, can be due to the following electrochemical reaction:



4. The anodic peak A_2 , which only appeared if the chemical species on the electrode was $\text{Cu}_2\text{O}_{(s)}$, can be due to the following electrochemical reaction:



Voltammetric study of Bi(III) and Bi(V) compounds in 10 M KOH media

Voltammograms of $\text{Bi}_2\text{O}_3(s)$

Figure 4 was obtained by scanning the potential from -0.275 V. When the first scan was cathodic, peak C_3 (-1.330 V) appeared; in addition, peak A_3 (-0.594 V) appeared in the return anodic scan, as shown in Fig. 4a.

The first anodic potential scan does not give any current signal. On the contrary, in the return cathodic scan, peak C_3 (-1.330 V) appeared, as well as peak A_3 (-0.594 V) in the second anodic scan, as can be seen in Fig. 4b. No signal appeared in subsequent potential scans.

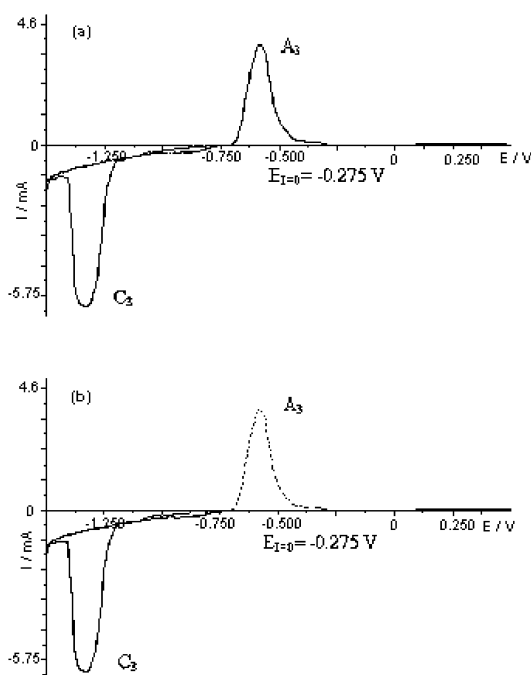


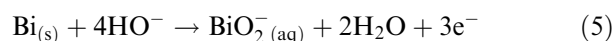
Fig. 4a,b Voltammograms of Bi_2O_3 . **a** First scan towards negative potential values. **b** First scan towards positive potential values. Full line: first cyclic scan; dashed line: second cyclic scan

Voltammograms of $\text{NaBiO}_3(s)$

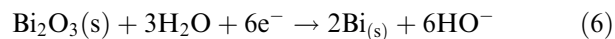
Voltammograms of $\text{NaBiO}_3(s)$, obtained from -0.170 V, are plotted in Fig. 5. In the first cathodic scan, cathodic peak C_4 (-1.100 V) as well as anodic peak A_3 (-0.594 V) were obtained, as can be seen in Fig. 5a. In Fig. 5b, at the first anodic scan, no signal was observed. Nevertheless, peaks C_4 (-1.100 V) and A_3 (-0.594 V) were obtained in the return cathodic scan and in the second anodic scan, respectively. No signal appeared in subsequent cyclic scans.

The obtained experimental results permitted us to deduce the following electrochemical processes:

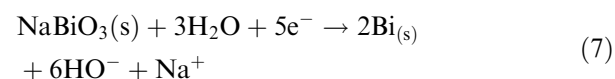
5. Anodic peak A_3 , which appeared at the same potential value in the voltammograms of both compounds, can be due to the following process:



6. Cathodic peak C_3 , which was only observed in the case of $\text{Bi}_2\text{O}_3(s)$, must correspond to the following electrochemical process:



7. Cathodic peak C_4 , which only appeared when the species on the electrode was $\text{NaBiO}_3(s)$, must correspond to the following electrochemical reaction:



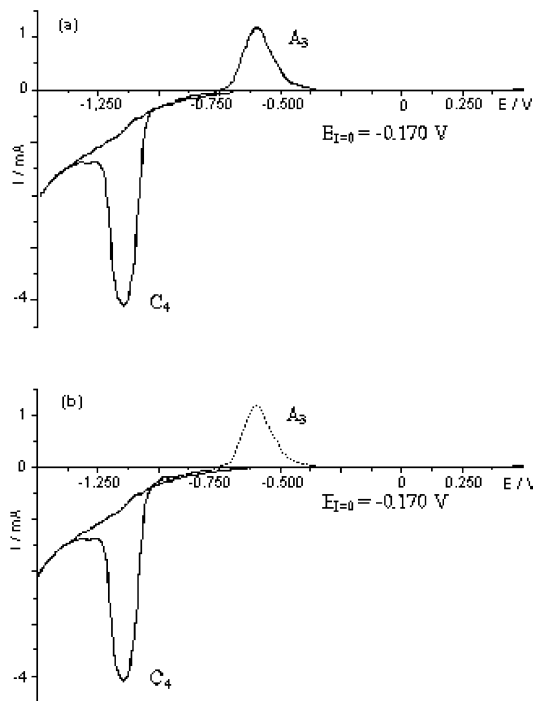


Fig. 5a,b Voltammograms of NaBiO_3 . **a** First scan towards negative potential values. **b** First scan towards positive potential values. *Full line*: first cyclic scan; *dashed line*: second cyclic scan

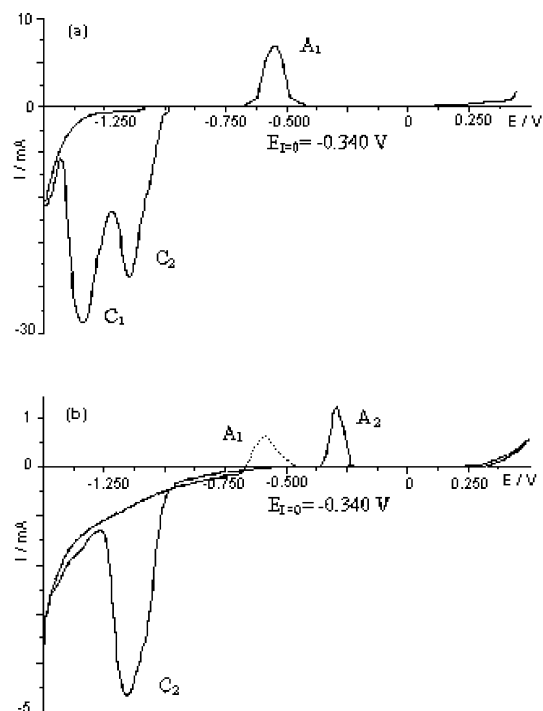


Fig. 6a,b Voltammograms of $\text{Cu}_2\text{O} + \text{CuO}$. **a** First scan towards negative potential values. **b** First scan towards positive potential values. *Full line*: first cyclic scan; *dashed line*: second cyclic scan

Voltammetric study of binary mixtures of copper and bismuth compounds in KOH media

In order to characterize high transition temperature superconductors by the use of voltammetry of immobilized microparticles, all binary mixtures of the different compounds of Cu(I), Cu(II), Bi(III) and Bi(V) were prepared and studied. Voltammograms of mixtures have been recorded as individual compounds.

Voltammograms of $\text{Cu}_2\text{O}_{(s)} + \text{CuO}_{(s)}$

In Fig. 6, voltammograms of the mixtures are shown, obtained by scanning the potential from -0.340 V . In Fig. 6a, peaks C_1 and C_2 , due to Cu(I) and Cu(II), respectively, appeared. In Fig. 6b, peak A_2 , corresponding to the oxidation of $\text{Cu}_2\text{O}_{(s)}$, and peak C_2 , due to the reduction of $\text{CuO}_{(s)}$, are shown. As a conclusion, we can affirm that it is possible to identify each solid compound in the mixture.

Voltammograms of $\text{Bi}_2\text{O}_3_{(s)} + \text{NaBiO}_3_{(s)}$

Figure 7 corresponds to voltammograms of mixtures obtained by scanning the potential from -0.190 V . Both voltammograms show the appearance of peaks C_3 and C_4 , corresponding respectively to Bi(III) and Bi(V), so it

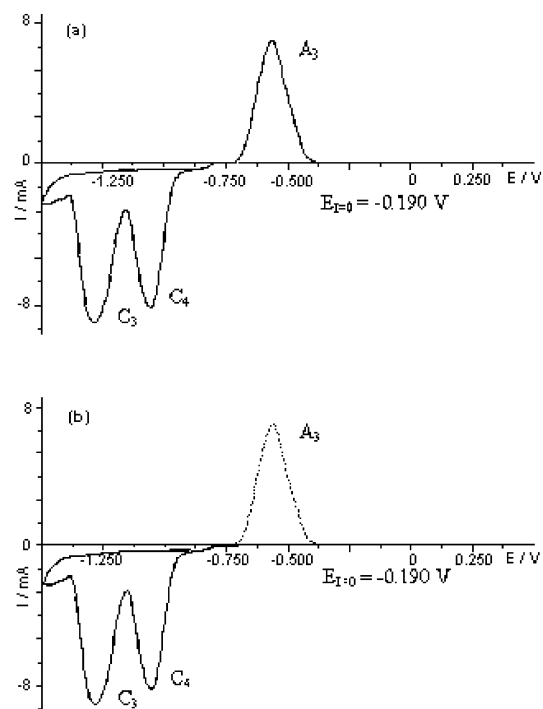


Fig. 7a,b Voltammograms of $\text{Bi}_2\text{O}_3 + \text{NaBiO}_3$. **a** First scan towards negative potential values. **b** First scan towards positive potential values. *Full line*: first cyclic scan; *dashed line*: second cyclic scan

is possible to confirm the presence of each compound in this mixture.

Voltammograms of $\text{Bi}_2\text{O}_3(\text{s}) + \text{Cu}_2\text{O}(\text{s})$

In Fig. 8, voltammograms of the mixture of these solids are plotted. These voltammograms were obtained by scanning the potential from -0.355 V. Figure 8a shows the characteristic peaks C_1 and C_3 for Cu(I) and Bi(III), respectively, and in Fig. 8b, anodic peak A_2 , due to the oxidation of $\text{Cu}_2\text{O}(\text{s})$, and cathodic peak C_3 , corresponding to the reduction of Bi(III), are shown. Therefore it is possible to confirm the presence of each compound in this mixture.

Voltammograms of $\text{Bi}_2\text{O}_3(\text{s}) + \text{CuO}(\text{s})$

In Fig. 9, voltammograms of $\text{Bi}_2\text{O}_3(\text{s})$ and $\text{CuO}(\text{s})$ compounds, obtained by scanning the potential from -0.250 V, are shown. In both voltammograms, peaks C_2 and C_3 , characteristic of Cu(II) and Bi(III), respectively, appeared. Therefore it is possible to identify each compound in this mixture.

Voltammograms of $\text{NaBiO}_3(\text{s}) + \text{Cu}_2\text{O}(\text{s})$

In Fig. 10, voltammograms of the mixture of these solids are plotted. These voltammograms were obtained by scanning the potential from -0.350 V. Figure 10a shows

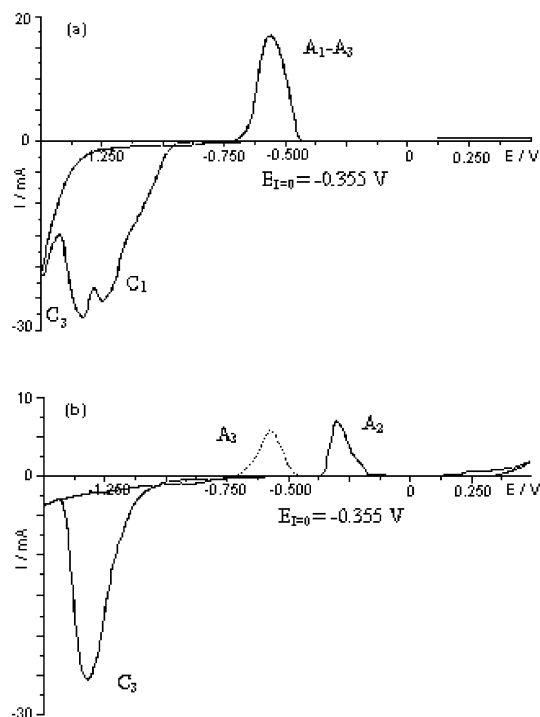


Fig. 8a,b Voltammograms of $\text{Bi}_2\text{O}_3 + \text{Cu}_2\text{O}$. **a** First scan towards negative potential values. **b** First scan towards positive potential values. *Full line*: first cyclic scan; *dashed line*: second cyclic scan

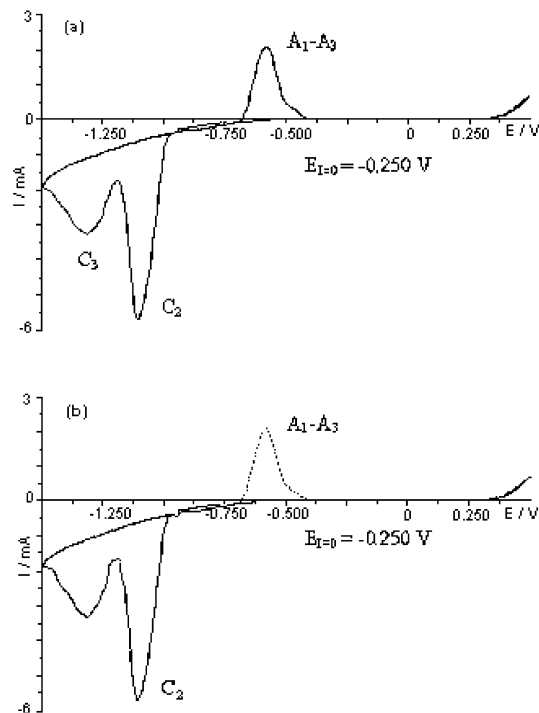


Fig. 9a,b Voltammograms of $\text{Bi}_2\text{O}_3 + \text{CuO}$. **a** First scan towards negative potential values. **b** First scan towards positive potential values. *Full line*: first cyclic scan; *dashed line*: second cyclic scan

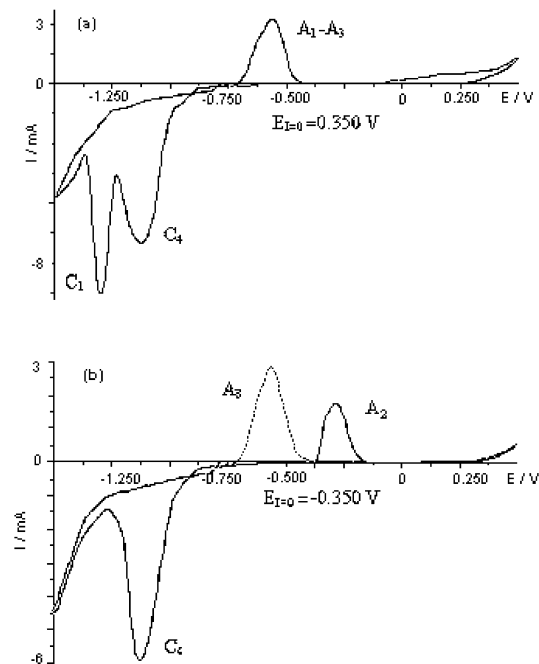


Fig. 10a,b Voltammograms of $\text{NaBiO}_3 + \text{Cu}_2\text{O}$. **a** First scan towards negative potential values. **b** First scan towards positive potential values. *Full line*: first cyclic scan; *dashed line*: second cyclic scan

peaks C_1 and C_4 for Cu(I) and Bi(V), respectively, and in Fig. 10b, anodic peak A_2 , due to the oxidation of $\text{Cu}_2\text{O}(\text{s})$, and cathodic peak C_4 , corresponding to the

reduction of $\text{NaBiO}_3(\text{s})$, are shown. Thus, in this mixture the identification of these compounds is also possible.

Voltammograms of $\text{NaBiO}_3(\text{s}) + \text{CuO}(\text{s})$

Figure 11 corresponds to the mixture of Bi(V) and Cu(II), obtained by starting the potential from -0.180 V , where an important superposition of signals, concerning cathodic peaks C_2 and C_4 , respectively occurred, as well as that of anodic peaks A_1 and A_2 . This result shows that, in this mixture, it is not possible to identify each chemical compound by this technique.

Voltammetric study of the superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.44}$ in 10 M KOH media

The voltammograms of the three superconductors obtained by potential scans from 0.02 V ($\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$), 0.00 V ($\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$) and 0.05 V ($\text{YBa}_2\text{Cu}_3\text{O}_{6.44}$) are shown in Figs. 12, 13 and 14, respectively.

When the first scan was started in the cathodic direction, as can be seen in Figs. 12a, 13a and 14a, peaks M_1 , M_2 and M_3 were obtained, as well as peak N_1 in the following anodic scan. When the first scan was anodic (Figs. 12b, 13b and 14b), no signal was observed. However, in the return cathodic scan, peaks M_1 , M_2 and M_3 appeared; in addition, peak N_1 was obtained in the

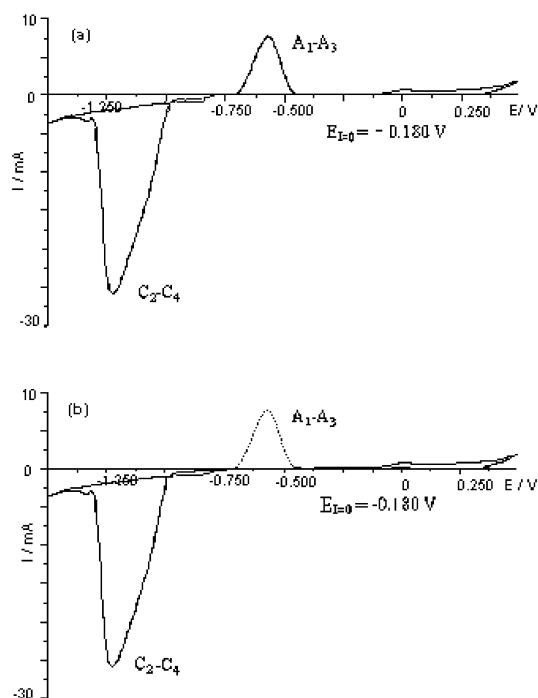


Fig. 11a,b Voltammograms of $\text{NaBiO}_3 + \text{CuO}$. **a** First scan towards negative potential values. **b** First scan towards positive potential values. *Full line*: first cyclic scan; *dashed line*: second cyclic scan

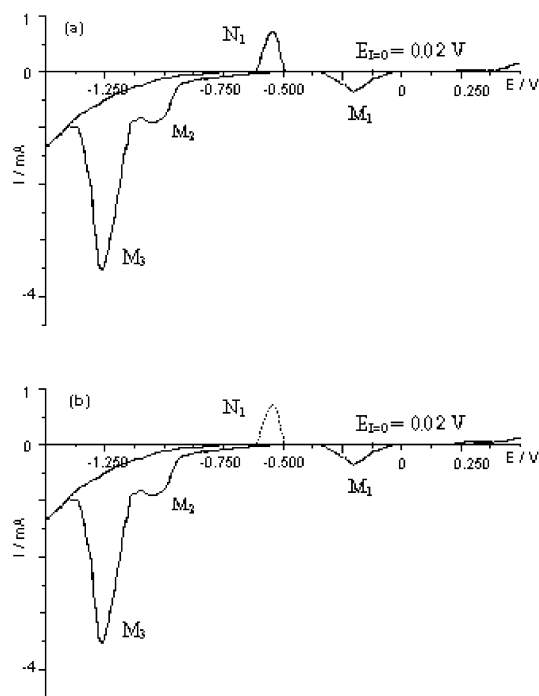


Fig. 12a,b Voltammograms of $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$. **a** First scan towards negative potential values. **b** First scan towards positive potential values. *Full line*: first cyclic scan; *dashed line*: second cyclic scan

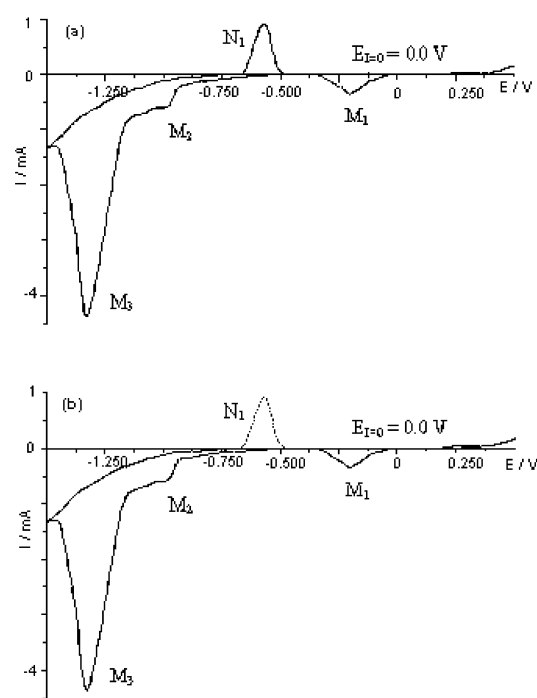


Fig. 13a,b Voltammograms of $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$. **a** First scan towards negative potential values. **b** First scan towards positive potential values. *Full line*: first cyclic scan; *dashed line*: second cyclic scan

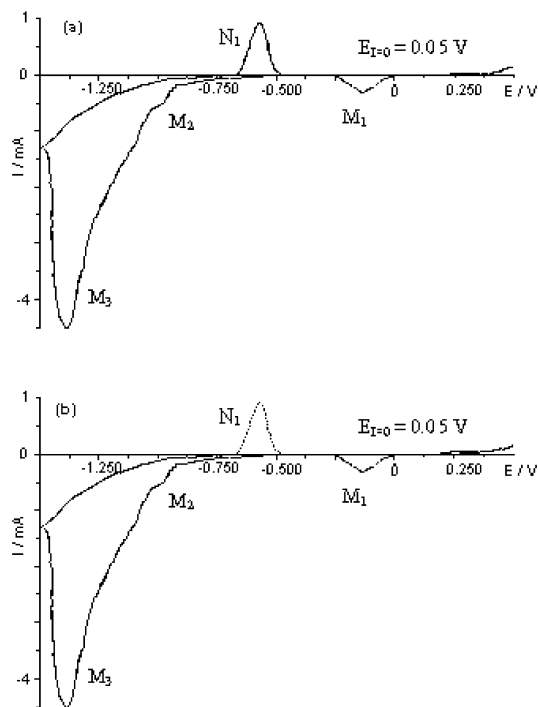


Fig. 14a,b Voltammograms of $\text{YBa}_2\text{Cu}_3\text{O}_{6.44}$. **a** First scan towards negative potential values. **b** First scan towards positive potential values. *Full line*: first cyclic scan; *dashed line*: second cyclic scan

second anodic scan, but no signals appeared in subsequent cyclic potential scans. The peak potential values for each superconductor are shown in Table 1.

By comparing the superconductor voltammograms with the one obtained with copper oxide mixtures, we can come to the following conclusions:

1. The appearance of peaks M_2 and M_3 at potential values near those of peaks C_1 and C_2 , characteristic of Cu(I) and Cu(II) oxides, respectively, confirms the presence of these cations in this superconductor.
2. The open circuit potential of the superconductors is a higher value than those obtained for the oxides and for the mixtures. This accounts for the absence of peak A_2 due to the anodic oxidation of Cu(I), because this appears at negative potentials.
3. Peak M_1 , which only appeared in the case of the superconductors, corresponds to the presence of Cu(III) in the solid.

Therefore the superconductor voltammograms show the presence of Cu(I) and Cu(II) as well as the presence of Cu(III).

Table 1 The peak potential values in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductors

Superconductor	M_1	M_2	M_3	N_1
$\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$	-0.202 V	-1.038 V	-1.267 V	-0.548 V
$\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$	-0.202 V	-0.987 V	-1.327 V	-0.567 V
$\text{YBa}_2\text{Cu}_3\text{O}_{6.44}$	-0.125 V	-0.985 V	-1.394 V	-0.567 V

Voltammetry study of the superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ in 10 M KOH

Voltammograms obtained from -0.150 V are shown in Fig. 15. When the first potential scan was carried out towards the cathodic potential, a broad signal, K_1 , appeared between -0.968 V to -1.180 V (Fig. 15a), as well as peak K_2 (-1.317 V). In the anodic return scan, peak L_1 (-0.570 V) also appeared.

When the first potential scan was started in the anodic direction (Fig. 15b), no signal was obtained. However, on the return cathodic scan, peaks K_1 and K_2 appeared as well as peak L_1 in the second anodic scan. No signal appeared in subsequent cyclic scans.

By comparing these voltammograms with those of the different mixtures of copper and bismuth compounds, the following aspects were deduced:

1. It is possible that Cu(I) and Bi(V) were not present in the superconductor, because no signal for these chemical species appeared in the voltammograms.
2. Peaks K_1 and K_2 appeared at potential values near those of the characteristic peaks C_2 and C_3 due to Cu(II) and Bi(III), respectively, confirming the presence of these cations in this superconductor. However, peak K_1 was observed with a different shape, possibly due to the structure of the superconductor and/or a little amount of Cu(II) that probably took part in the redox process.

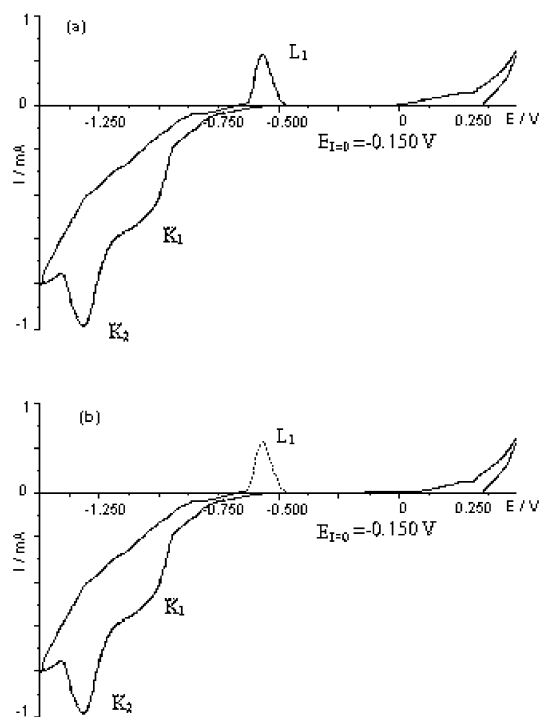


Fig. 15a,b Voltammograms of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. **a** First scan towards negative potential values. **b** First scan towards positive potential values. *Full line*: first cyclic scan; *dashed line*: second cyclic scan

Therefore, the superconductor voltammograms show the presence of Cu(II) and Bi(III).

Conclusions

In this paper, the carbon paste electrode was utilized in special conditions to carry out an electroanalytical study of different solids by the use of the voltammetry of immobilized microparticles with linear and cyclic potential scans.

By comparing these results with the ones obtained by using a composite electrode of carbon paste with an electrolytic binder [12, 13], it can be concluded that the voltammetry of immobilized microparticles furnishes only voltammograms due to solid compounds initially incorporated into the electrode or electrochemically generated during the electrochemical process.

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